An Efficient Generation and Selective Aldol Reaction of the Boryl Enolates of *N,N*-Dialkyl-2,3,3,3-tetrafluoropropanamides[1)]

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(Received November 25, 1989)

Successive treatment of *N,N*-dialkyl-2,3,3,3-tetrafluoropropanamide with dibutylboryl triflate at 0 °C and with ethyldiisopropylamine at −10 °C resulted in clean formation of the boryl enolate of the amide, which readily reacted with various aldehydes to give the corresponding 2-fluoro-3-hydroxy-2-trifluoromethylalkanamides with high threo-selectivity and in good yields.

Introduction of a fluorine and/or perfluoroalkyl (R_f) group into organic compounds often brings about their unique properties, particularly biological and physiological activities, and hence a variety of fluorine-containing pharmaceuticals and agrochemicals have been synthesized.[2)] In this connection, there are many studies directed towards the development and applications of various types of fluorinated building blocks.[3)] Recent reports demonstrated that monofluoro[4)] and difluoro enolates[5)] of carbonyl compounds are very intriguing in their high versatilities in organic synthesis.[6)] The enolates carrying an R_f group, especially trifluoromethyl, on the carbon terminus in their ambident anionic structure should be one of the most potent candidates for synthesizing biochemically interesting compounds. However, only a few examples dealing with such species have hitherto appeared in the literature.[7)] As part of our continuing efforts to extend the chemistry of fluorinated enolates,[5a,b,e,8)] we intended to develop the method for the generation of metal enolates of *N,N*-dialkyl-2,3,3,3-tetrafluoropropanamides (**1**). In this paper, we wish to disclose the results on the boryl enolates of **1** as well as their aldol reaction with carbonyl compounds leading predominantly to *threo*-2-fluoro-3-hydroxy-2-trifluoromethylalkanamides (**4**).[9)]

Results and Discussion

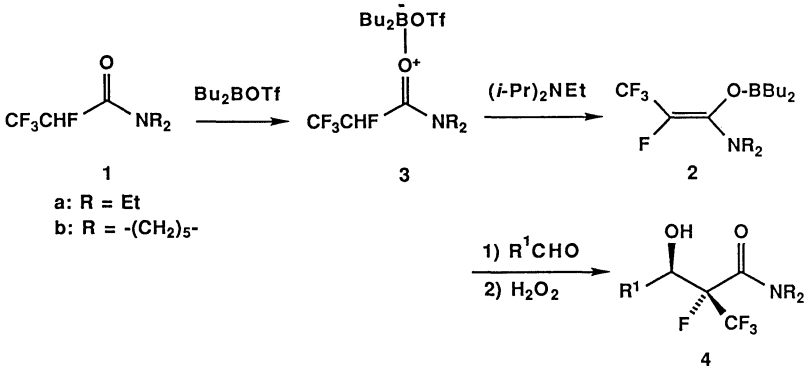
The starting amides **1a** and **1b** could easily be prepared in high yields by alkaline hydrolysis of an adduct[11)] of hexafluoropropene and diethylamine or piperidine. When the amide **1a** was treated with butyllithium or lithium diisopropylamide at low temperature (−78 °C), a very complex mixture of products resulted probably from β-elimination of fluoride ion from a transient lithium enolate followed by further side-reactions.[12)]

This undesirable β-elimination would be suppressed by increasing covalency of a bond between the enolate oxygen and a counter metal, which may render the enolate stable. A more important factor to prevent the β-elimination would be that the counter metal coordinates strongly to the amide carbonyl oxygen in precedence to α-deprotonation with a base. These considerations led us to examine the reaction of **1** using dibutylboryl triflate capable of effectively interacting with an oxygen moiety.[13)] Thus, sequential treatment of **1a** with dibutylboryl triflate and ethyldiisopropylamine in dichloromethane at 0 to −10 °C was found to produce efficiently the desired enolate **2a**

Table 1. ^{19}F NMR Data of the Amide **1a** and the Enolate **2a**

Compound	δ_{CF_3}[a)]	δ_{CF}[a)]
1a	−75.7 (dd, J=12.2, 6.1 Hz)	−199.4 (dq, J=45.2, 12.2 Hz)
3a	−75.4 (dd, J=13.4, 6.1 Hz)	−200.1 (dq, J=45.2, 13.4 Hz)
2a	−70.4 (d, J=12.2 Hz)	−201.2 (q, J=12.2 Hz)

a) Expressed in ppm downfield from internal $CFCl_3$.

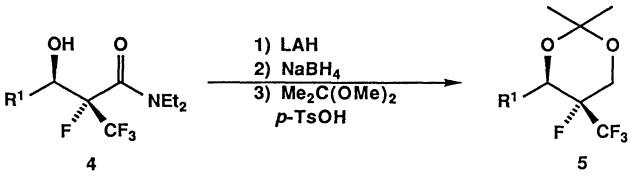


Scheme 1.

as a single stereoisomer (Scheme 1). Monitering each sequence of this reaction by ^{19}F NMR gave us the following observations: The signals of **1a** were slightly shifted on addition of dibutylboryl triflate. When the amine was added to this reaction mixture, both fluorine-hydrogen vicinal (6.1 Hz) and geminal (45.2 Hz) couplings disappeared and one set of signals appeared as doublet and quartet peaks. These are strongly suggestive of the intermediacy of the expected species **2a** and **3a**, whose spectral data are listed in Table 1 along with the starting amide **1a**. The *E*-geometry of the enolate was determined on the basis of the stereochemical outcome in the aldol reaction of **2a**, which will be discussed later. The enolate **2a** was not so stable above 0 °C. Trimethylsilyl triflate and 9-borabicyclo[3.3.1]non-9-yl triflate were ineffective for the present reaction. Among the tertiary amines examined, such as ethyldiisopropylamine, triethylamine, and 1,8-diazabicyclo[5.4.0]undec-7-ene, ethyldiisopropylamine gave the best results.

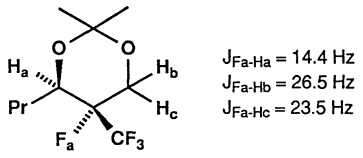
When the enolate **2a** thus generated was allowed to react with butanal at −10 °C, *N*,*N*-diethyl-2-fluoro-3-hydroxy-2-trifluoromethylhexanamide (**4a**) was obtained as a 94:6 mixture of threo and erythro isomer[9] in 88% yield (Entry 1). Other aldehydes including α,β-unsaturated and aromatic aldehydes reacted smoothly with **2a** to afford the corresponding hydroxy alkanamides **4** in good to excellent yields and with high threo-selectivity.[9] Ketones like 3-pentanone or cyclohexanone failed to react in spite of the amounts of the reagents or the reaction time being varied. The amide **1b** also participated well in the aldol reaction under the same reaction conditions (Entry 11). Noteworthy is the fact that the present aldol reaction proceeded efficiently at −10 °C but was extremely sluggish at −78 °C. It should be noted that the above-mentioned control of the reaction temperatures as well as exact use of molar ratios of the reagents are required to carry out the reaction of **2** successfully. Table 2 summarizes the results of these reactions.

The stereochemistry of the hydroxy amides **4** was assigned to be threo by converting them into the corresponding acetonides **5** (Scheme 2) and analyzing their ^{19}F and ^{1}H NMR spectra, since it has been reported that the syn fluorine-hydrogen vicinal couplings in 2-fluoro-1,3-diol systems are smaller than those in the anti relationship.[14] The pertinent fluorine-hydrogen vicinal couplings are shown below for the threo isomers of **5a** and **5g**.



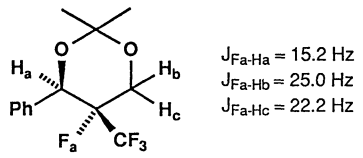
Scheme 2.

It has been well recognized[15] that the aldol reactions of boryl enolates proceed via a chair-like six-membered cyclic transition state;[16] *Z*-enolate gives erythro-aldols and *E*-enolate affords threo-aldols stereospecifically. This stereochemical correlation may safely be applied to the reaction between the fluorinated boryl enolates **2** and carbonyl compounds. Thus, the facts that **2** generated in-situ was a single geometrical isomer and led to highly preferential formation of the threo isomers **4** enabled us to assign the *E* geometry to the enolate **2**.



$J_{Fa\text{-}Ha}$ = 14.4 Hz
$J_{Fa\text{-}Hb}$ = 26.5 Hz
$J_{Fa\text{-}Hc}$ = 23.5 Hz

5a



$J_{Fa\text{-}Ha}$ = 15.2 Hz
$J_{Fa\text{-}Hb}$ = 25.0 Hz
$J_{Fa\text{-}Hc}$ = 22.2 Hz

5g

Table 2. Aldol Reaction of Amides **1** with Aldehydes

Entry	Amide	Aldehyde	Yield[a]		Isomer ratio[b]
			%		Threo : Erythro
1	**1a**	$CH_3CH_2CH_2CHO$	**4a**,	88	94: 6
2		$(CH_3)_2CHCHO$	**4b**,	86	92: 8
3		$(CH_3)_3CCHO$	**4c**,	74	85:15
4		(*E*)-CH_3CH=$CHCHO$	**4d**,	85	93: 7
5		(*E*)-CH_3CH=$C(CH_3)CHO$	**4e**,	82	92: 8
6		(*E*)-C_6H_5CH=$CHCHO$	**4f**,	86	100: 0
7		C_6H_5CHO	**4g**,	84	93: 7
8		*p*-$CH_3C_6H_4CHO$	**4h**,	78	100: 0
9		*p*-$CH_3OC_6H_4CHO$	**4i**,	82	94: 6
10		*p*-ClC_6H_4CHO	**4j**,	76	100: 0
11	**1b**	C_6H_5CHO	**4k**,	89	95: 5

a) The yields refer to pure isolated products. b) Determined by ^{19}F NMR.

Key features of the present reaction are summarized as follows: The boryl enolates **2** can be generated selectively in an *E* form from readily available *N,N*-dialkyl-2,3,3,3-tetrafluoropropanamides (**1**) and they undergo the aldol reaction with a wide variety of aldehydes with high threo-selectivity.[9] This method will serve as a general and effective route to *threo*-2-fluoro-3-hydroxy-2-trifluoromethylalkanamides (**4**), which are difficult to prepare by other methods.

Experimental

General. ^{1}H NMR spectra were recorded with a Varian EM-390, XL-200, or a JEOL JNM-PMX60SI spectrometer (TMS, δ). ^{19}F NMR spectra were obtained on a JEOL FX90Q computer-controlled spectrometer using trichlorofluoromethane ($CFCl_3$) as an internal standard. IR spectra were taken on a Shimadzu IR-400 or JASCO IR-810 spectrometer. Mass spectra were determined by using a Shimadzu QP-1000 GC-mass spectrometer at 20 eV. Column chromatography was carried out with silica gel (Wakogel C-200).

Solvents were freshly distilled prior to use. Aldehydes and ketones were distilled (or vacuum-distilled) from calcium hydride and stored under argon. All other chemicals were of reagent grade and, if necessary, were purified by a conventional manner.

Preparation of Amides 1a and 1b. Hexafluoropropene (17 ml, 180 mmol) was allowed to react with diethylamine (11.0 g, 150 mmol) in diethyl ether (50 ml) according to the reported procedure. The resulting crude adduct was treated with a saturated aqueous sodium hydrogencarbonate (20 ml) under cooling with an ice bath. The mixture was extracted with diethyl ether (30 ml×3) and the combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel to give **1a**[17] (24.7 g, 82%): IR (neat) 1671 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.28 (dq, J=46.4, 6.1 Hz, 1H), 3.40 (q, J=7.0 Hz, 4H), 1.25 (t, J=7.0 Hz, 3H), and 1.18 (t, J=7.0 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−75.86 (dd, J=12.2, 6.1 Hz, 3F) and −199.28 (dq, J=46.4, 12.2 Hz, 1F). The amide **1b** was prepared in a similar manner: 92%; ^{1}H NMR ($CDCl_3$) δ=5.35 (dq, J=32.9, 6.1 Hz, 1H), 3.8—2.9 (br s, 4H), and 1.9—1.4 (br s, 6H); ^{19}F NMR ($CDCl_3$) δ=−75.83 (dd, J=13.4, 6.1 Hz, 3F) and −198.8 (dq, J=32.9, 13.4 Hz, 1F).

Aldol Reaction of Amides 1 with Aldehydes. Typical Procedure. To a solution of **1a** (0.201 g, 1.0 mmol) in dichloromethane (5 ml) was added a dichloromethane solution (1 mol dm^{-3}) of dibutylboryl triflate (1.1 ml, 1.1 mmol) at 0 °C under argon. After 10 min, ethyldiisopropylamine (0.155 g, 1.2 mmol) was added to the reaction mixture at −10 °C. After stirring for 15 min, butanal (0.080 g, 1.1 mmol) was added. The resultant mixture was stirred for 30 min at −10 °C, and poured into a mixture of phosphate buffer (pH 7, 4 ml), 30% aqueous hydrogen peroxide (1 ml), and ice. After being stirred for 1 h at 0 °C, this mixture was added to an aqueous solution of sodium sulfite (1.23 g) and stirred at room temperature. The mixture was extracted with diethyl ether (30 ml×3). The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude residue was purified by silica-gel column chromatography to give *N,N*-diethyl-2-fluoro-3-hydroxy-2-trifluoromethylhexanamide (**4a**) (0.240 g): IR (neat) 3388 (O-H) and 1639 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.40 (br d, J=20.8 Hz, 1H), 3.7—3.1 (m, 4H), 2.6 (br s, 1H), 1.8—1.4 (m, 4H), 1.23 (t, J=6.4 Hz, 3H), 1.15 (t, J=6.4 Hz, 3H), and 0.94 (t, J=5.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.69 (d, J=4.9 Hz, 3F) and −184.43 (dq, J=20.8, 4.9 Hz, 1F); MS m/z (rel intensity) 273 (M^+, 2.3) and 72 (100). Found: C, 48.54; H, 7.19; F, 27.65%. Calcd for $C_{11}H_{19}F_4NO_2$: C, 48.35; H, 7.01; F, 27.81%.

***N,N*-Diethyl-2-fluoro-3-hydroxy-4-methyl-2-trifluoromethylpentanamide (4b):** IR (neat) 3426 (O-H) and 1639 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.34 (br d, J=25.6 Nz, 1H), 3.8—3.1 (m, 4H), 2.4—1.7 (br s, 1H), and 1.4—0.7 (m, 12H); ^{19}F NMR ($CDCl_3$) δ=−73.10 (d, J=4.9 Hz, 3F) and −186.82 (dq, J=25.6, 4.9 Hz, 1F) for the threo isomer, −74.93 (d, J=8.6 Hz, 3F) and −172.40 (m, 1F) for the erythro isomer; MS m/z (rel intensity) 258 (M^+-CH_3, 2) and 201 (100). Found: C, 48.49; H, 6.92; F, 27.60%. Calcd for $C_{11}H_{19}F_4NO_2$: C, 48.35; H, 7.01; F, 27.81%.

***N,N*-Diethyl-2-fluoro-3-hydroxy-4,4-dimethyl-2-trifluoromethylpentanamide (4c):** IR (neat) 3458 (O-H) and 1638 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.42 (d, J=31.7 Hz, 1H), 3.8—3.0 (m, 5H), 1.23 (t, J=6.4 Hz, 3H), 1.13 (t, J=6.4 Hz, 3H), and 1.03 (s, 9H); ^{19}F NMR ($CDCl_3$) δ=−72.68 (d, J=3.67 Hz, 3F) and −187.56 (dq, J=31.7, 3.7 Hz, 1F) for the threo isomer, −75.70 (d, J=8.5 Hz, 3F) and −168.83 (m, 1F) for the erythro isomer; MS m/z (rel intensity) 287 (M^+, 0.5) and 57 (100). Found: C, 50.31; H, 7.39; F, 26.62%. Calcd for $C_{12}H_{21}F_4NO_2$: C, 50.17; H, 7.37; F, 26.45%.

***(E)*-*N,N*-Diethyl-2-fluoro-3-hydroxy-2-trifluoromethyl-4-hexenamide (4d):** IR (neat) 3422 (O-H) and 1639 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.2—5.1 (m, 2H), 4.85 (dd, J=22.0, 6.6 Hz, 1H), 3.7—3.0 (m, 4H), 3.0—2.3 (br s, 1H), 1.71 (d, J=5.4 Hz, 3H), 1.22 (t, J=6.4 Hz, 3H), and 1.14 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.65 (d, J=4.9 Hz, 3F) and −183.43 (dq, J=22.0, 4.9 Hz, 1F) for the threo isomer, −74.49 (d, J=7.3 Hz, 3F) for the erythro isomer; MS m/z (rel intensity) 271 (M^+, 7) and 72 (100). Found: C, 48.55; H, 6.04; F, 27.83%. Calcd for $C_{11}H_{17}F_4NO_2$: C, 48.71; H, 6.32; F, 28.02%.

***(E)*-*N,N*-Diethyl-2-fluoro-3-hydroxy-4-methyl-2-trifluoromethyl-4-hexenamide (4e):** IR (neat) 3436 (O-H) and 1639 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.39 (q, J=6.4 Hz, 1H), 4.86 (d, J=25.6 Hz, 1H), 3.7—2.9 (m, 4H), 2.6—1.9 (br s, 1H), 1.65 (s, 3H), 1.59 (d, J=6.4 Hz, 3H), 1.17 (t, J=6.4 Hz, 3H), and 1.09 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.64 (d, J=3.7 Hz, 3F) and −185.27 (dq, J=25.6, 3.7 Hz, 1F) for the threo isomer, −75.09 (d, J=7.3 Hz, 3F) and −174.52 (m, 1F) for the erythro isomer; MS m/z (rel intensity) 285 (M^+, 5) and 202 (100). Found: C, 50.68; H, 6.79; F, 26.53%. Calcd for $C_{12}H_{19}F_4NO_2$: C, 50.52; H, 6.71; F, 26.64%.

***(E)*-*N,N*-Diethyl-2-fluoro-3-hydroxy-5-phenyl-2-trifluoromethyl-4-pentenamide (4f):** IR (neat) 3454 (O-H) and 1638 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.20 (s, 5H), 6.66 (d, J=16.0 Hz, 1H), 6.09 (dd, J=16.0, 6.4 Hz, 1H), 5.01 (dd, J=19.5, 6.4 Hz, 1H), 3.7—3.1 (m, 4H), 3.1—2.0 (br s, 1H), 1.16 (t, J=6.4 Hz, 3H), and 1.05 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.50 (d, J=4.9 Hz, 3F) and −182.42 (dq, J=19.5, 4.9 Hz, 1F); MS m/z (rel intensity) 333 (M^+, 5) and 72 (100). Found: C, 57.84; H, 5.96; F, 22.73%. Calcd for $C_{16}H_{19}F_4NO_2$: C, 57.65; H, 5.75; F, 22.80%.

***N,N*-Diethyl-2-fluoro-3-hydroxy-3-phenyl-2-trifluoro-**

methylpropanamide (4g): IR (neat) 3426 (O-H) and 1640 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.6—7.1 (m, 5H), 5.54 (d, J=23.2 Hz, 1H), 3.4—2.6 (m, 5H), 0.89 (t, J=6.4 Hz, 3H), and 0.83 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−74.82 (d, J=7.3Hz, 3F) and −186.70 (dq, J=23.2, 7.3 Hz, 1F) for the threo isomer; MS m/z (rel intensity) 307 (M^+, 0.5) and 72 (100). Found: C, 54.86; H, 5.61; F, 24.58%. Calcd for $C_{14}H_{17}F_4NO_2$: C, 54.72; H, 5.58; F, 24.73%.

***N,N*-Diethyl-2-fluoro-3-hydroxy-3-(*p*-tolyl)-2-trifluoromethylpropanamide (4h):** IR (neat) 3432 (O-H) and 1636 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.22 (d, J=8.4 Hz, 2H), 7.00 (d, J=8.4 Hz, 2H), 5.47 (d, J=24.4 Hz, 1H), 3.4—2.5 (m, 5H), 2.31 (s, 3H), 0.92 (t, J=6.4 Hz, 3H), and 0.84 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.35 (d, J=3.7 Hz, 3F) and −186.89 (dq, J=24.4, 3.7 Hz, 1F) for the threo isomer; MS m/z (rel intensity) 321 (M^+, 0.1) and 72 (100). Found: C, 56.22, H, 5.81; F, 23.83%. Calcd for $C_{15}H_{19}F_4NO_2$: C, 56.07; H, 5.96; F, 23.65%.

***N,N*-Diethyl-2-fluoro-3-hydroxy-3-(4-methoxyphenyl)-2-trifluoromethylpropanamide (4i):** IR (neat) 3436 (O-H) and 1636 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.21 (d, J=9.2 Hz, 2H), 6.70 (d, J=9.2 Hz, 2H), 5.44 (d, J=24.4 Hz, 1H), 3.72 (s, 3H), 3.4—2.6 (m, 5H), 0.92 (t, J=6.4 Hz, 3H), and 0.86 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.38 (d, J=3.7 Hz, 3F) and −187.12 (dq, J=24.4, 3.7 Hz, 1F) for the threo isomer, −74.71 (d, J=8.6 Hz, 3F) for the erythro isomer; MS m/z (rel intensity) 327 (M^+, 0.1) and 72 (100). Found: C, 53.69; H, 5.77; F, 22.25%. Calcd for $C_{15}H_{19}F_4NO_3$: C, 53.41; H, 5.68; F, 22.53%.

***N,N*-Diethyl-2-fluoro-3-(4-chlorophenyl)-3-hydroxy-2-trifluoromethylpropanamide (4j):** IR (neat) 3406 (O-H) and 1636 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.4—7.1 (m, 4H), 5.52 (d, J=23.2 Hz, 1H), 3.4—2.7 (m, 5H), 0.96 (t, J=6.4 Hz, 3H), and 0.88 (t, J=6.4 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−72.32 (d, J=3.7 Hz, 3F) and −186.60 (dq, J=23.2, 3.7 Hz, 1F); MS m/z (rel intensity) 343 (0.1), 341 (M^+, 0.3), and 72 (100). Found: C, 49.36; H, 4.80; F, 22.37%. Calcd for $C_{14}H_{16}ClF_4NO_2$: C, 49.21; H, 4.72; F, 22.24%.

1-(2-Fluoro-3-hydroxy-3-phenyl-2-trifluoromethylpropionyl)piperidine (4k): ^1H NMR ($CDCl_3$) δ=7.5—7.1 (br s, 5H), 5.49 (dd, J=22.6, 6.0 Hz, 1H), 3.7—2.9 (m, 5H), and 1.7—0.6 (m, 6H); ^{19}F NMR ($CDCl_3$) δ=−72.21 (d, J=3.7 Hz, 3F) and −183.4 (dd, J=22.6, 3.7 Hz, 1F). Found: C, 56.57; H, 5.48; F, 23.89%. Calcd for $C_{15}H_{17}F_4NO_2$: C, 56.42; H, 5.37; F, 23.80%.

Preparation of 5-Fluoro-2,2-dimethyl-4-phenyl-5-trifluoromethyl-1,3-dioxane (5g). The aldol **4g** (0.307 g, 1.0 mmol) was reduced successively with lithium aluminium hydride (1 mol dm^{-3} tetrahydrofuran solution, 1.0 ml, 1.0 mmol) in dry tetrahydrofuran (5 ml) at −10° and with sodium borohydride (0.114 g, 3.0 mmol) in methanol (5 ml) at room temperature. A usual workup of the reaction mixture gave the crude diol, which was treated with 2,2-dimethoxypropane (1.04 g, 10 mmol) in the presence of *p*-toluenesulfonic acid monohydrate (0.019 g, 0.1 mmol) in refluxing tetrahydrofuran (10 ml) for 24 h. The mixture was poured into a mixture of ice and a saturated aqueous sodium hydrogencarbonate and was extracted with diethyl ether (20 ml×3). Drying, filtration, concentration, and column chromatography gave **5g** (0.161 g, 57.9% from **4g**): IR (neat) 1380, 1271, 1229, 1215, 1201, 1183, 1165, 1131, 1102, 1049, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.5—7.3 (m, 5H), 5.13 (dq, J=15.2, 1.8 Hz, 1H), 4.24 (dd, J=25.0, 13.6 Hz, 1H), 4.04 (ddq, J=22.2, 13.6, 1.2 Hz, 1H), 1.52 (s, 3H), and 1.51 (s, 3H); ^{19}F NMR ($CDCl_3$) δ=−76.30 (d, J=8.5 Hz, 3F) and −170.17 (dddq, J=25.0, 22.2, 15.2, 8.5 Hz, 1F); MS m/z (rel intensity) 278 (M^+, 3) and 60 (100).

5-Fluoro-2,2-dimethyl-4-propyl-5-trifluoromethyl-1,3-dioxane (5a) was prepared in the same manner: IR (neat) 2986, 2960, 2936, 1379, 1261, 1229, 1208, 1189, 1153, 1122, 1091, and 1029 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.10 (dd, J=26.5, 14.0 Hz, 1H), 3.90 (ddq, J=23.5, 14.0, 1.3 Hz, 1H), 4.0—3.8 (m, 1H), 1.9—1.5 (m, 4H), 1.42 (s, 3H), 1.38 (s, 3H), and 0.98 (t, J=7.0 Hz, 3H); ^{19}F NMR ($CDCl_3$) δ=−76.68 (d, J=6.1 Hz, 3F) and −173.16 (dddq, J=26.5, 23.5, 14.4, 6.1 Hz, 1F); MS m/z (rel intensity) 244 (M^+, 0.1) and 60 (100).

References

1) Presented at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 1989, Abstr., No. 8D-2l2.

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